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10/019492

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING SUBMISSION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

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Nederlandsch Octrooibureau
Scheveningseweg 82
P.O. Box 29720
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Date of mailing (day/month/year) 26 February 2002 (26.02.02)	
Applicant's or agent's file reference BO 42433 AS	**IMPORTANT NOTIFICATION**
International application No. PCT/NL00/00462	International filing date (day/month/year) 30 June 2000 (30.06.00)
International publication date (day/month/year) 04 January 2001 (04.01.01)	Priority date (day/month/year) 30 June 1999 (30.06.99)
Applicant COOPERATIE COSUN U.A. et al	

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
3. An **asterisk(*)** appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
4. The **letters "NR"** appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
30 June 1999 (30.06.99)	1012482	NL	10 Augu 2000 (10.08.00)

The International Bureau of WIPO
34, chemin des Colombettes
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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
BO 42433 RJ		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/NL00/00462	30/06/2000	30/06/1999
International Patent Classification (IPC) or national classification and IPC C11D3/39		
Applicant COOPERATIE COSUN N.A. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 7 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 1 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
29/01/2001	~~17.09.2001~~ 05. 12. 01
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Culmann, J-C Telephone No. +49 89 2399 8487

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL00/00462

I. Basis of the report

1. With regard to the **lements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:
Description, pages:

1-8	as originally filed				
Claims, No.:					
1-10	as received on	26/06/2001	with letter of	26/06/2001	
Drawings, sheets:					
1/1	as originally filed				

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   - ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
   - ☐ the language of publication of the international application (under Rule 48.3(b)).
   - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   - ☐ contained in the international application in written form.
   - ☐ filed together with the international application in computer readable form.
   - ☐ furnished subsequently to this Authority in written form.
   - ☐ furnished subsequently to this Authority in computer readable form.
   - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   - ☐ the description, pages:
   - ☐ the claims, Nos.:

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-7
	No:	Claims	8-10
Inventive step (IS)	Yes:	Claims	1-7
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-10
	No:	Claims	

2. Citations and explanations
   see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

HarCor#2

Preliminary remark

1. The claims may be put into three groups:

   - the first group related to the use of specific acylated fructans as a bleach activator;
   - the second group relates to a process;
   - the third group relates to partially acylated fructans defined by their solubility.

2. It may be noted that the process claims are not restricted to the obtention of those products, the use of which is claimed in claims 1 to 7; as is the subject-matter of claim 10. *Stricto-sensu*, there is a lack of unity between the subject-matter of claims 1 to 7, claims 8 to 9, and 10.

   Since only the subject-matter of claims 1 to 7 is novel and inventive, it makes no sense to raise an objection of lack of unity of invention.

   The Applicant will have nevertheless to bear this point in mind upon entering the regional phase.

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step and industrial applicability

1. The Applicant has established by means of comparisons that partially acylated fructans having a degree of substitution with acyl groups of 0.4 to 2.5 and a degree of substitution of less than 0.5 with other substituents were better bleach activators (in terms of solubility, percentage of acetyl groups available for the bleaching step) than i) fructans having a degree of substitution with acyl groups of 3.0 and ii) acylated fructans having a degree of substitution of more than 0.2 with other substituents (carboxymethyl groups).

Accordingly, the Applicant has established that his partially acylated fructans were better bleach activators than e.g. those fructans taught by D1 i.e. EP-A-0 814 088, wherein the degree of substitution with substituents other than acyl groups is 1 (see Example 8 of this citation, which is very close from the first activator investigated by the Applicant, see the table in the present application).

The subject-matter of claim 1 is not only novel (because of the degrees of substitution) over EP-A-0 814 088, but also inventive in the sense that the improved properties of the activator, the use of which is claimed in claims 1 to 7, were not taught nor derivable from the prior art, alone or in combination.

2. The subject-matter of claims 8 and 9 lacks novelty over the document D2 i.e. "E.BERGHOFER et all, Chemical Modification of Chicory Root Inulin, Studies in Plant Science, NL, Amsterdam, Elsevier edit., vol. 3, pages 135-142 (1993)", more particularly over the conditions under which inulin was acetylised (pH adjusted to 7.5, temperature set at 20°C).

Under 2.1 of D2 it is specified that inulin is derivatized with a mixed acetic/adipic acid anhydride at a pH of 7.5 and at a temperature of 20°C. While adipoyl is certainly produced, it cannot be conceived that no acetyl derivative is also produced.

While it may be that the objection results from an inadequate wording of the claims (which are not directed to a product within the scope of claim 1), the present assessment has to be made in respect with the claims as they are currently drafted.

Said subject-matter is also not inventive, because the effects discussed above under 1. (solubility, percentage of acetyl groups available for the bleaching step) are related to the degrees of substitution. These do not appear in the wording of the incriminated claims. The effects discussed above obviously relate to (at most) a sub-group of chemicals, not to all the chemicals conceivably made by the process of claims 8 and 9.

However, as previously suggested, should the Applicant restrict the scope of the claimed process to the producing of partially acylated fructans as defined in claims 1 to 7, then such a restricted process could be seen by a regional patent office as novel and involving an inventive step (because of properties of the resulting material). The process and the use claims would also be unitary by the same token.

3. The subject-matter of claim 10 lacks novelty over D3 i.e. EP-A-0 792 888: at least in Examples 1, 13, and 14 inulin is acetylised/propionylised to yield a derivative having a solubility of at least 10g/l (or 1% by weight) as established in Table 1 of D3).

The bleach activating property is in this respect irrelevant, since claim 10 addresses chemicals *per se*. It is doubtful that said subject-matter can be amended in such a way as to make it fulfil the requirements of Article 33(2) EPC and of Rule 13 EPC or an equivalent article before any regional patent office.

Incidentally, the subject-matter could be objected pursuant to Article 5PCT (or any regional equivalent) because the skilled reader ignores how to produce all the compounds encompassed by this claim.

VII. Certain defects in the international application.

The requirements of Rule 5.1 a) ii) PCT are not met, the document D2 is not identified in the description and the relevant background art disclosed therein is not briefly discussed.

VIII. Certain observations on the international application.

Parts of the subject-matter of claims 2, 4 and 5 are not supported by the

description:

- C_1-C_6 acyl groups in claim 2 (the description merely specifies upper limits, and isolated individuals, not the specified range as such);
- "in particular 4-30" in claim 4.

Claims

1. Use of a partially acylated fructan having a degree of substitution with acyl groups of 0.4 - 2.5 and a degree of substitution of at most 0.2 with other substituents as a bleach activator.

2. Use according to Claim 1, wherein the fructan is acylated with C_1-C_6 acyl groups.

3. Use according to Claim 1 or 2, wherein the fructan is acylated with a degree of substitution of 0.6 - 1.8.

4. Use according to one of Claims 1 - 3, wherein the fructan has an average chain length of 3 - 60, in particular 4 - 30.

5. Use according to one of Claims 1 - 4, wherein the other substituents are carboxymethyl groups.

6. Use according to one of Claims 1 - 5, wherein the fructan is inulin.

7. Use according to one of Claims 1 - 6, wherein the fructan has been acylated with acetyl and/or propionyl groups.

8. A process of producing an acylated fructan or fructan derivative by acylation of the fructan or derivative thereof with a reactive acyl derivative of a monocarboxylic acid, characterised in that the acylation is carried out in an aqueous medium at a pH of between 7 and 9.

9. A process according to Claim 8, characterised in that the acylation is carried out at a temperature of between 0 and 40 °C.

10. Partially acylated fructan obtainable using the method according to Claim 8 or 9, which has a solubility in water of at least 1 g/l, in particular of at least 2 g/l.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(51) International Patent Classification[7]: C11D 3/39, 3/22, D06L 3/02, C08B 37/18, C07H 15/04

(21) International Application Number: PCT/NL00/00462

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(30) Priority Data:
1012482 30 June 1999 (30.06.1999) NL

(71) Applicant *(for all designated States except US)*: **CO-OPERATIE COSUN U.A.** [NL/NL]; P.O. Box 1308, NL-4700 BH Roosendaal (NL).

(72) Inventors; and
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(74) Agent: **JORRITSMA, Ruurd**; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/00771 A1

(54) Title: BLEACH ACTIVATOR BASED ON INULIN

(57) Abstract: The invention relates to the use of a partially acylated fructan, in particular a partially acylated inulin, having a degree of substitution with acyl groups of 0.4-2.5 and a degree of substitution of at most 0.2 with other substituents, as a bleach activator. The solubility and efficiency of these derivatives is better than that of comparable products such as completely acylated derivatives and carboxylated derivatives. The derivatives are prepared by acylation in an aqueous medium under controlled pH.

INTERNATIONAL SEARCH REPORT

nation: pplication No
PCT/NL 00/00462

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/39 C11D3/22 D06L3/02 C08B37/18 C07H15/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D D06L C08B C07H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BERGHOFER E ET AL: "CHEMICAL MODIFICATION OF CHICORY ROOT INULIN" , STUDIES IN PLANT SCIENCE,NL,AMSTERDAM, ELSEVIER, VOL. VOL. 3, PAGE(S) 135-142 XP002031614	8,9
A	page 136, line 1 -page 137, line 5 page 137, line 35 -page 138, line 13	10
A	EP 0 792 888 A (SUEDZUCKER AG) 3 September 1997 (1997-09-03) cited in the application claims 1-11,15-18 examples 14,20 page 4, line 28 - line 30	1-4,6-10

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 September 2000	06/10/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Neys, P

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

·nation· ·plication No
PCT/NL 00/00462

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 01200 A (BEGHIN SAY ERIDANIA) 21 January 1993 (1993-01-21) claims examples page 1, line 16 - line 24 page 4, line 29 - line 34	1-9
A	EP 0 814 088 A (SUEDZUCKER AG) 29 December 1997 (1997-12-29) cited in the application claims example 8 page 2, line 47 -page 3, line 16 page 3, line 47 - line 58	1-7
A	WO 96 34934 A (SOLVAY INTEROX LTD) 7 November 1996 (1996-11-07) claims examples page 3, line 14 - line 29 page 6, line 14 -page 8, line 30 page 13, line 8 - line 14	1-7

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Information: Application No
PCT/NL 00/00462

Patent document cited in search report	Publication date	Patent family member(s)	Publication dat
EP 0792888 A	03-09-1997	DE 19607847 C	20-11-1997
		JP 9328501 A	22-12-1997
		US 5877144 A	02-03-1999
WO 9301200 A	21-01-1993	FR 2678937 A	15-01-1993
		AU 2360292 A	11-02-1993
		EP 0547217 A	23-06-1993
EP 0814088 A	29-12-1997	DE 19624345 A	08-01-1998
		US 6063752 A	16-05-2000
WO 9634934 A	07-11-1996	AU 5343996 A	21-11-1996
		BR 9608256 A	02-02-1999
		CA 2220221 A	07-11-1996
		EP 0840777 A	13-05-1998
		JP 11504376 T	20-04-1999
		US 6020295 A	01-02-2000
		ZA 9603498 A	13-11-1996

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(74) Agent: **JORRITSMA, Ruurd**; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).

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(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

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WO 01/00771 A1

(54) Title: BLEACH ACTIVATOR BASED ON INULIN

(57) Abstract: The invention relates to the use of a partially acylated fructan, in particular a partially acylated inulin, having a degree of substitution with acyl groups of 0.4-2.5 and a degree of substitution of at most 0.2 with other substituents, as a bleach activator. The solubility and efficiency of these derivatives is better than that of comparable products such as completely acylated derivatives and carboxylated derivatives. The derivatives are prepared by acylation in an aqueous medium under controlled pH.

Bleach activator based on inulin

The invention relates to the use of fructan derivatives as a bleach activator.

In addition to a bleaching agent, such as a peroxide, percarbonate or perborate, a bleach activator is usually needed for bleaching, for example, textile materials in the washing process. The most widely used bleach activator is tetraacetylethylenediamine (TAED). The disadvantage of TAED is that it is moderately to poorly biodegradable and is thus an undesired constituent in waste water. The use of acetylated sucrose (degree of substitution 4.5 - 7), in particular hexa-acetylsucrose, as bleach activator is disclosed in EP-A 492 000. Peracetylated sugar acids (sucrose, maltose, lactose) having a bleach-activating action are disclosed in EP-A 731 161. Acetylated carboxymethylinulin derivatives which are said to have a bleach-activating action are described in EP-A 814 088.

It has been found that acylated fructans and fructan derivatives are outstandingly suitable as a bleach activator, having an activity comparable to that of TAED and having much better biodegradability. The acylated fructans and fructan derivatives to be used according to the invention have an average degree of substitution (in acyl groups) of 0.4 - 2.5, preferably of 0.6 - 1.8 and preferentially of 0.8 - 1.6. Surprisingly the bleach-activating action of the acylated inulins according to the invention is also found to be better than that of the comparable acylated carboxymethylinulins according to EP-A 814 088. The acyl groups in the acylated fructan according to the invention are preferably derived from monocarboxylic acids and can be acetyl, propionyl, butyryl and higher alkanoyl groups (for example up to C12, in particular up to C6) and optionally formyl, alkenoyl, pyruvyl and benzoyl groups and the like, including mixtures, for example of acetyl and propionyl groups, both within a molecule (acetylpropionylfructan) and of different substances (acetylfructan and propionylfructan), as long as the total or average degree of substitution is within the set limits.

Acylated inulin is known per se from EP-A 792 888. The acylated inulins described in this publication preferably have a degree of substitution of 0.5 or less and are proposed as a surfactant.

Here fructans are understood to be all oligosaccharides and polysaccharides which have a majority of anhydrofructose units. The fructans can have a polydisperse chain length distribution and can be straight-chain or branched. The fructans comprise both products obtainable directly from a vegetable or other source and the products in which the average

chain length has been modified (increased or reduced) by fractionation, enzymatic hydrolysis or synthesis. The fructans have an average chain length (= degree of polymerisation, DP) of at least 3, up to about 1000, in particular of 3 to 60 monosaccharide units. Preferably the fructan contains mainly β-2,1 bonds, as in inulin. Inulin can be obtained, inter alia, from chicory, dahlias and Jerusalem artichokes.

Acylated reduced fructans can also be used. Reduced fructans are fructans in which reducing end groups (usually fructose groups) have been reduced, for example using sodium borohydride or using hydrogen in the presence of a transition metal catalyst.

Furthermore, chemically or physically modified fructans can serve as the basis for acylated derivatives. The chemical modification preferably corresponds to a degree of substitution in the modification of less than 0.5, in particular less than 0.2. The modification can be, for example, an alkyl group, hydroxyalkyl group, carboxyalkyl group, alkoxy-carbonylalkyl group, carboxyl group, alkoxycarbonyl group, aminoalkyl group or acylamino group.

Various methods of preparation for acylated fructans and fructan derivatives are available. Reaction of carboxymethylinulin (DS 1.0) with excess acetic anhydride in the presence of sodium acetate at 120 °C (analogous to Example 12 in EP 792 888) yields a product which has a relatively low content of acetyl groups (DS acetyl = 0.78). Virtually complete acetylation in good yield (89%) can be achieved by carrying out this reaction at 140 °C (analogous to the R.L. Whistler method, *Methods in Carbohydrate Chemistry,* Vol II, 211-212).

It has been found that the reaction of fructans and fructan derivatives with acetic anhydride in water at controlled pH is an exceptionally suitable method for the preparation of partially acylated fructans and fructan derivatives. The pH is kept constant at a value of between 7 and 9, preferably of about 8, during the reaction. The reaction temperature is between 0 and 80 °C, preferably between 0 and 40 °C. This method results in the formation of partially acylated fructans and fructan derivatives in good yield (85 - 95%) and with a high reaction efficiency (50 - 75%); the reaction efficiency is defined as the degree of acylation determined divided by the maximum degree of acylation calculated on the basis of the quantity of acylating agent (DS_{det}/DS_{theor} x 100%). Instead of acid anhydrides it is also possible to use other reactive acyl derivatives, such as acid halides, reactive esters, in particular vinyl esters, such as vinyl acetate and vinyl propionate, for the acylation.

It has been found that the partial acetylation of carboxymethylinulin (CMI) in a mixture of acetic acid, acetic anhydride and sulphuric acid analogous to EP 814 088 leads only to a product in low yield (41%) and with a low reaction efficiency (8%).

The bleach activator property is determined on the basis of the quantity of peracetic acid that can be liberated from the product. It has been found that the bleach activator properties of the (partially) acylated fructans and fructan derivatives depend on the method by which the acylation has been carried out. The best characteristics are found when the acylation is carried out in water at controlled pH (Table 1).

The acetylation of CMI with acetic anhydride, acetic acid and sulphuric acid (EP 814 088) or acetic anhydride and sodium acetate at elevated temperature yields products which have poor solubility in water and low activity as bleach activator.

Partial acylation of CMI by reaction of CMI with acetic anhydride in water at controlled pH gives products which have adequate solubility in water and better results in the bleach activator test. The solubility in water is appreciably higher than that of corresponding products prepared in accordance with the prior art. The invention also relates to such an acylation method and to the products having a solubility in water of at least 1g/l which are obtainable in this way.

Surprisingly it has been found that the lower the degree of substitution of carboxymethyl groups in partially acetylated CMI the better is the action as bleach activator. Preferably partially acetylated CMI having a degree of substitution of carboxymethyl groups of less than 0.2 is used.

For partially acetylated inulin (no carboxyl groups present) it is found that the solubility of the products obtained is good up to a DS_{acetyl} of 2.0. The bleach activator action of these compounds is better than that of partially acetylated CMI. The action of partially acetylated inulin having a DS of 1.7 approaches the action of TAED and SORMAN. A possible explanation for these results is that the bleach activator action appears to be determined by the solubility in water and the availability of the acetyl groups. The mol % peracetate formed is a measure of the availability of the acetyl groups. Poor solubility in water gives low availability of the acetyl groups for peracetate formation.

Table 1: Solubility and bleach activator action of partially acetylated CMI, partially acetylated inulin, SORMAN and TAED on the basis of amount of peracetate liberated

DS (carboxymethyl)	DS (acetyl)	Synthesis method[1]	Solubility (%)	Peracetate formed (mol%)[2]	mol peracetate/ kg product
1	0.51	A	<0.1	39	0.8
1	1.05	B	<0.1	17	0.5
1	1.5	C	<0.1	20	1.0
0.2	0.66	D	>5	67	2.1
0.85	0.73	D	>5	51	1.4
1.5	1.12	D	>5	16	0.5
0	0.58	D	>5	73	2.3
0	1.01	D	>5	74	3.7
0	1.53	D	>5	73	5.0
0	1.71	D	>5	71	5.2
0	3.0	C	<0.1	4	0.1
0	0	-	10	-	-
1	0	-	50	-	-
Comparison:					
TAED[3]	4.0	-	0.1	45	7.9
SORMAN[4]	6.0	-	0.1	44	6.0

1: A: AcOH/Ac_2O/H_2SO_4, 50 °C, 3 hours; B: Ac_2O/NaOAc, 120 °C, 4 hours; C: Ac_2O/NaOAc, 140 °C, 4 hours; D: Ac_2O/H_2O, pH 8, 25 °C.

2: 100 x number of mols of peracetate formed / total number of mols of acetyl groups in product.

3: tetraacetylethylenediamine

4: mixture of peracetylsorbitol and peracetylmannitol (EP 525 239)

It can clearly be seen from Table 1 that the presence of carboxyl groups in the inulin molecule has an adverse effect on the availability of the acetyl groups for peracetate formation. The quantity of peracetate/kg product is also adversely affected as a result.

For partially acetylated inulin the availability of the acetyl groups is virtually independent of the degree of acetylation to a maximum DS of approximately 2. This means that the quantity of peracetate per kg product increases virtually in proportion with the degree of substitution (Figure 1). Above DS 2 the solubility, and thus also the availability of acetyl groups for peracetate formation, decreases again.

Compared with TAED and SORMAN, the availability of the acetyl groups in partially acetylated inulin is substantially higher and therefore if the degree of acetylation is sufficiently high the peracetate formation per kg approaches that of TAED. The high availability of acetyl groups in the partially acetylated inulin appears to be a unique property of this inulin derivative. Figure 1 shows a plot of the number of mols of peracetic acid per kg product against the DS_{acetyl}.

Example 1: *Acetylation of inulin, DS 1.0*

50 ml water was added to 30 g inulin (185 mmol, chicory, DP ≈10), after which the mixture was homogenised and adjusted to pH 8 with 2M NaOH. 28 ml (296 mmol) acetic anhydride was added dropwise to the mixture at room temperature whilst the pH was kept at 8 using a pH-stat with the addition of 10M NaOH solution. The temperature was kept at 25 °C. 15 minutes after all the acetic anhydride had been added, the solution was diluted with water to a volume of approximately 500 ml and the pH was adjusted to 6. After standing overnight the precipitate was filtered off. The filtrate was purified by nanofiltration. The filtrate from the nanofiltration was concentrated (Rotavapor) and the residue was dried in a vacuum oven at 70 °C. Yield: 36.25 g (95%) with a DS (degree of substitution) in acetyl of 1.01. Reaction efficiency: 63%. The product had a surface tension (1% g/g solution at 30 °C) of 47.78 ± 0.06 mN/m. The product released an amount of peracetate (in mol%, determined in accordance with the procedure as described in Example 9) of 74 mol% or 3.7 mol peracetate per kg product.

Example 2: *Acetylation of inulin, DS 0.5*

Example 1 was repeated, but using 15 ml (159 mmol) acetic anhydride. DS: 0.51; yield: 98%; reaction efficiency: 73%.

Example 3: *Acetylation of inulin, DS 1.5*

Example 1 was repeated, but using 58 ml (613 mmol) acetic anhydride. DS: 1.51; yield: 84%; reaction efficiency: 53%.

Example 4: *Acetylation of carboxymethylinulin*

218 g acetic anhydride was added dropwise to a solution of 150 g carboxymethylinulin (CMI, DS 0.88) in the course of 3 hours whilst the pH was kept at 8 using 10M NaOH and the temperature was kept at 25 °C. 15 minutes after all the acetic anhydride had been added the solution was diluted with water to a volume of approximately 2.3 l and the pH was adjusted to 6. After standing overnight the precipitate was filtered off. The filtrate was purified by electrodialysis. The product was concentrated (Rotavapor) and the residue was dried in a vacuum oven at 70 °C. Yield: 134.6 g (74%) with a DS (degree of substitution) in acetyl of 1.2. Reaction efficiency: 63%.

Example 5: *Acetylation of inulin with NaOAc in acetic anhydride at 140 °C*

A suspension of inulin (30 g) and sodium acetate (3 g) in acetic anhydride (150 ml) was heated (140 °C, 4 hours). The hot reaction mixture was poured into ice-water (approximately 2 l) and stirred overnight. The resulting precipitate was filtered off and dried in air. Yield: 47.2 g (89%). DS_{acetyl}: 3.0. Reaction efficiency: 38%.

Comparative Example A: *Acetylation of carboxymethylinulin in an acid medium*

A mixture of acetic anhydride (25 ml) and acetic acid (10 ml, 100%) was added dropwise to a solution of CMI (DS 1.0; 10 g) in acetic acid (50 ml, 100%) and concentrated sulphuric acid (0.3 ml) and the mixture was then stirred (3 hours, 50 °C). The solution was cooled and filtered through a glass filter. The residue was washed (400 ml acetone/water (3:1)). After removing acetone from the combined filtrates (Rotavapor) the product was desalinated by means of nanofiltration. The residue was freeze-dried. Yield: 5.8 g (53%). DS_{acetyl}: 0.49. Reaction efficiency: 8%.

Comparative Example B: *Acetylation of CMI DS 1.0 with NaOAc and acetic anhydride at 120 °C*

A suspension of CMI (10 g, DS 1.0) and sodium acetate (0.5 g) in acetic anhydride (50 ml) was heated (120 °C, 4 hours). After cooling to room temperature the precipitate was removed by means of filtration and the residue was washed with acetic anhydride. The filtrate was concentrated under vacuum (Rotavapor). The residue was then taken up in water and freeze-dried. Yield: 7.7 g (68%). DS_{acetyl}: 0.78. Reaction efficiency: 7%.

Comparative Example C: *Acetylation of CMI (DS 1.0) with NaOAc in acetic anhydride at 140 °C*

Example 5 was carried out using CMI (10 g, DS 1.0), sodium acetate (0.5 g) and acetic anhydride (50 ml). Yield: 27.7 g (73%). DS_{acetyl}: 1.5. Reaction efficiency: 13%.

Example 6: *Propionylation of inulin*

50 ml water was added to 30 g inulin (185 mmol, chicory, DP ≈ 10), after which the mixture was homogenised and the pH was adjusted to 8 with 10M NaOH. 50 ml (388 mmol) propionic anhydride was added dropwise to the mixture at room temperature whilst the pH was kept at 8 and the temperature was kept at 25 °C. After standing overnight the precipitate was separated off, rinsed with water and filtered off. The residue was dried in air. Yield 41.0 g (92%) with a DS (degree of substitution) in propionyl of 1.41. Reaction efficiency: 67%.

Comparative Example D: *Reproduction of Example 14 in EP-A 792 888*

15 g (0.09 mol) inulin was dissolved in 250 ml water. 12.3 ml (0.09 mol) propionic anhydride and 300 g Merck III ion exchanger (OH^- form) were added to this solution. The mixture was heated for 24 hours at 40 °C with stirring. The solution was filtered (Büchner) and the filtrate was evaporated. After adding 100 ml water, the mixture was filtered again. The filtrate was freeze-dried. The yield was so low (158 mg) that characterisation was dispensed with. Various attempts to improve the result (a: repetition; b: extract resin with water, evaporate extract as well; c: rinse resin with methanol, evaporate methanol fraction as well; d: lower pH from 11 to 6 after reaction) gave no improvement.

Example 7: *Bleach activator test procedure*

Mix the following solutions:

- 15 ml 0.6% hydrogen peroxide solution
- 10 ml saturated sodium pyrophosphate solution
- 10 ml 0.05% EDTA solution.
- Make up to 100 ml with demineralised water and heat to 30 °C.
- Add the heated mixture to an accurately weighed amount (75 - 90 mg) of bleach activator in a 600 ml glass beaker.
- Adjust the pH to 11.6 with 0.1 M NaOH solution.
- Precisely 4 minutes after the first addition add 30 ml 0.1% catalase solution.
- Adjust the pH to 10.5 with 0.5 M sulphuric acid solution and cool the solution to 0 - 3 °C.
- Precisely 6 minutes after the first addition add 15 ml 100% acetic acid solution and 15 ml 10% potassium iodide solution.
- Titrate the liberated iodine against a 0.1 M thiosulphate solution.

The mol% peracetic acid liberated from the bleach activator can be calculated from the quantity of thiosulphate solution required, 2 mmol thiosulphate corresponding to 1 mmol peracetic acid formed. The determinations were corrected for the loss of peracetic acid during the measurement. The correction factor for this loss is 1.10. The results of these determinations are given in Table 1.

Claims

1. Use of a partially acylated fructan having a degree of substitution with acyl groups of 0.4 - 2.5 and a degree of substitution of at most 0.2 with other substituents as a bleach activator.

2. Use according to Claim 1, wherein the fructan is acylated with C_1-C_6 acyl groups.

3. Use according to Claim 1 or 2, wherein the fructan is acylated with a degree of substitution of 0.6 - 1.8.

4. Use according to one of Claims 1 - 3, wherein the fructan has an average chain length of 3 - 60, in particular 4 - 30.

5. Use according to one of Claims 1 - 4, wherein the other substituents are carboxymethyl groups.

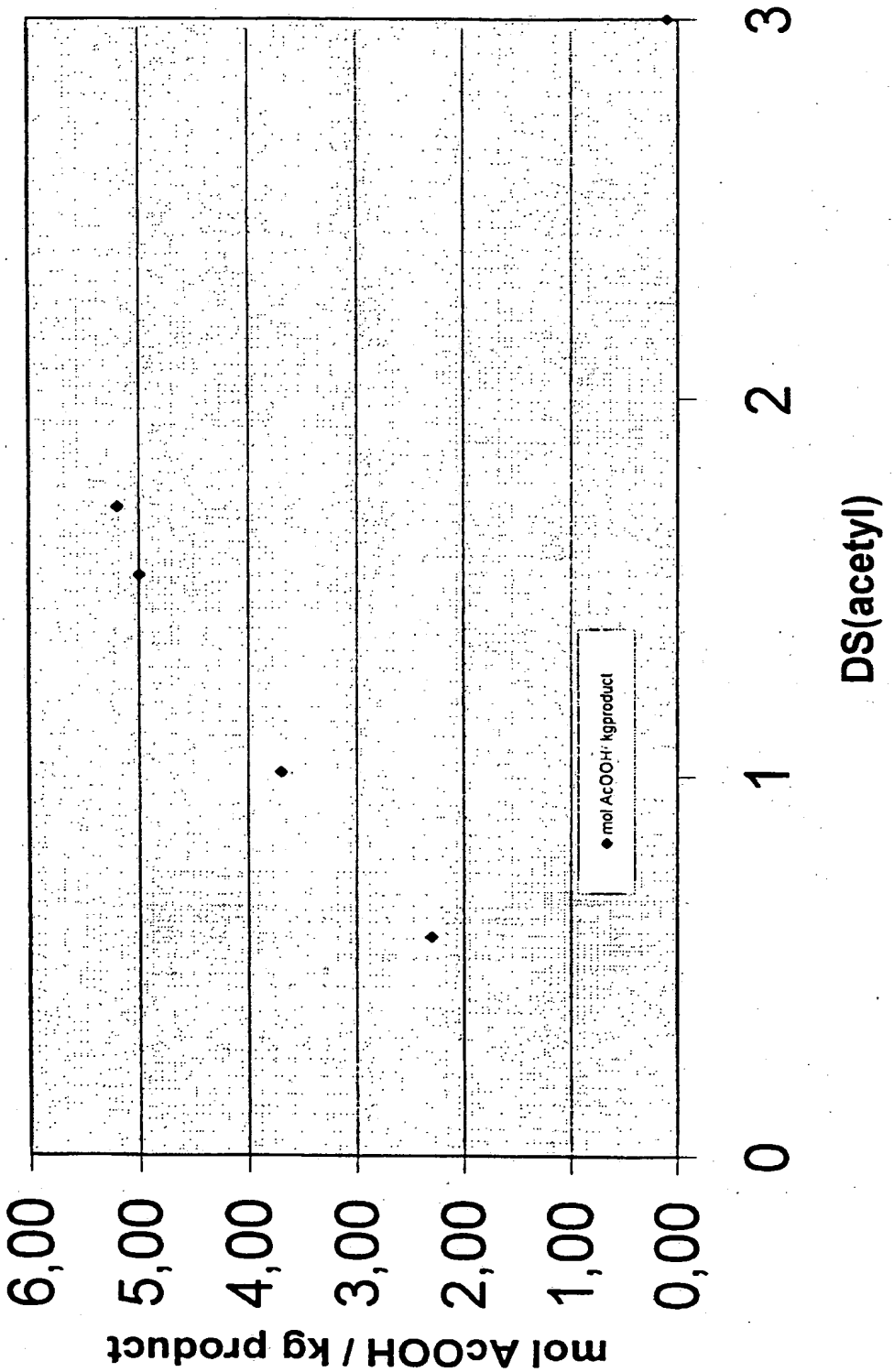
6. Use according to one of Claims 1 - 5, wherein the fructan is inulin.

7. Use according to one of Claims 1 - 6, wherein the fructan has been acylated with acetyl and/or propionyl groups.

8. A process of producing an acylated fructan or fructan derivative by acylation of the fructan or derivative thereof with a reactive acyl derivative of a monocarboxylic acid, characterised in that the acylation is carried out in an aqueous medium at a pH of between 7 and 9.

9. A process according to Claim 8, characterised in that the acylation is carried out at a temperature of between 0 and 40 °C.

10. Partially acylated fructan obtainable using the method according to Claim 8 or 9, which has a solubility in water of at least 1 g/l, in particular of at least 2 g/l.


mol AcOOH / kg product
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0
1
2
3
DS(acetyl)
mol AcOOH/ kgproduct

27.07.00

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

PCT/NL 00/00462
International Application No.

International Filing Date 30 JUN 2000 (30.06.00)

BUREAU VOOR DE INDUSTRIËLE EIGENDOM
P.C.T. INTERNATIONAL APPLICATION

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference *(if desired) (12 characters maximum)* BO 42433 AS

Box No. I TITLE OF INVENTION

Bleach activator based on inulin

Box No. II APPLICANT

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

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Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

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☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ■ agent ☐ common representative

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Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

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- ☐ all designated States
- ☐ all designated States except the United States of America
- ☒ the United States of America only
- ☐ the States indicated in the Supplemental Box

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State *(that is, country)* of residence: The Netherlands (NL)

This person is applicant for the purposes of:
- ☐ all designated States
- ☐ all designated States except the United States of America
- ☒ the United States of America only
- ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

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State *(that is, country)* of residence: The Netherlands (NL)

This person is applicant for the purposes of:
- ☐ all designated States
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Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

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- ☒ applicant and inventor
- ☐ inventor only *(If this check-box is marked, do not fill in below.)*

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State *(that is, country)* of residence: The Nethelands (NL)

This person is applicant for the purposes of:
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- ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) *(mark the applicable check-boxes; at least one must be marked)*:

Regional Patent

- ■ AP **ARIPO Patent:** **GH** Ghana, **GM** Gambia, **KE** Kenya, **LS** Lesotho, **MW** Malawi, **SD** Sudan, **SL** Sierra Leone, **SZ** Swaziland, **TZ** United Republic of Tanzania, **UG** Uganda, **ZW** Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ■ EA **Eurasian Patent:** **AM** Armenia, **AZ** Azerbaijan, **BY** Belarus, **KG** Kyrgyzstan, **KZ** Kazakhstan, **MD** Republic of Moldova, **RU** Russian Federation, **TJ** Tajikistan, **TM** Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ■ EP **European Patent:** **AT** Austria, **BE** Belgium, **CH and LI** Switzerland and Liechtenstein, **CY** Cyprus, **DE** Germany, **DK** Denmark, **ES** Spain, **FI** Finland, **FR** France, **GB** United Kingdom, **GR** Greece, **IE** Ireland, **IT** Italy, **LU** Luxembourg, **MC** Monaco, **NL** Netherlands, **PT** Portugal, **SE** Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ■ OA **OAPI Patent:** **BF** Burkina Faso, **BJ** Benin, **CF** Central African Republic, **CG** Congo, **CI** Côte d'Ivoire, **CM** Cameroon, **GA** Gabon, **GN** Guinea, **GW** Guinea-Bissau, **ML** Mali, **MR** Mauritania, **NE** Niger, **SN** Senegal, **TD** Chad, **TG** Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT *(if other kind of protection or treatment desired, specify on dotted line)* .....

National Patent *(if other kind of protection or treatment desired, specify on dotted line)*:

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- ■ AZ Azerbaijan
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- ■ BB Barbados
- ■ BG Bulgaria
- ■ BR Brazil
- ■ BY Belarus
- ■ CA Canada
- ■ CH and LI Switzerland and Liechtenstein
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- ■ KE Kenya
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- ■ KR Republic of Korea
- ■ KZ Kazakhstan
- ■ LC Saint Lucia
- ■ LK Sri Lanka
- ■ LR Liberia
- ■ LS Lesotho
- ■ LT Lithuania
- ■ LU Luxembourg
- ■ LV Latvia
- ■ MA Morocco
- ■ MD Republic of Moldova
- ■ MG Madagascar
- ■ MK The former Yugoslav Republic of Macedonia
- ■ MN Mongolia
- ■ MW Malawi
- ■ MX Mexico
- ■ NO Norway
- ■ NZ New Zealand
- ■ PL Poland
- ■ PT Portugal
- ■ RO Romania
- ■ RU Russian Federation
- ■ SD Sudan
- ■ SE Sweden
- ■ SG Singapore
- ■ SI Slovenia
- ■ SK Slovakia
- ■ SL Sierra Leone
- ■ TJ Tajikistan
- ■ TM Turkmenistan
- ■ TR Turkey
- ■ TT Trinidad and Tobago
- ■ TZ United Republic of Tanzania
- ■ UA Ukraine
- ■ UG Uganda
- ■ US United States of America
- ■ UZ Uzbekistan
- ■ VN Viet Nam
- ■ YU Yugoslavia
- ■ ZA South Africa
- ■ ZW Zimbabwe

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet:

- ■ DZ Algeria
- ■ AG Antigua and Barbuda

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. *(Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)*

Box No. VI PRIORITY CLAIM ☐ Further priority claims are indicated in the Supplemental Box.

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is: national application: country	regional application:* regional Office	international application: receiving Office
item (1) 30. 06. 99 30 June 1999	1012482	The Netherlands		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) *(only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office)* identified above as item(s): 1

** Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.*

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) *(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):* ISA / EPA

Request to use results of earlier search; reference to that search *(if an earlier search has been carried out by or requested from the International Searching Authority):*

Date *(day/month/year)* 10 February Number SN 33485 NL Country *(or regional Office)* The Netherlands

Box No. VIII CHECK LIST; LANGUAGE OF FILING

This international application contains the following **number of sheets**:

request	: 4
description (excluding sequence listing part)	: 8
claims	: 1
abstract	: 1
drawings	: 1
sequence listing part of description	:
Total number of sheets	: 15

This international application is **accompanied by** the item(s) marked below:

1. ☒ fee calculation sheet
2. ☐ separate signed power of attorney
3. ☐ copy of general power of attorney; reference number, if any:
4. ☐ statement explaining lack of signature
5. ☐ priority document(s) identified in Box No. VI as item(s):
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☒ other *(specify)*: Copy search report

Figure of the drawings which should accompany the abstract:

Language of filing of the international application: English

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

JORRITSMA, R.

Nederlandsch Octrooibureau, The Hague, 30 June 2000

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1. Date of actual receipt of the purported international application: 30. 06. 00 30 JUN 2000	2. Drawings: ☒ received: ☐ not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	6. ☐ Transmittal of search copy delayed until search fee is paid.

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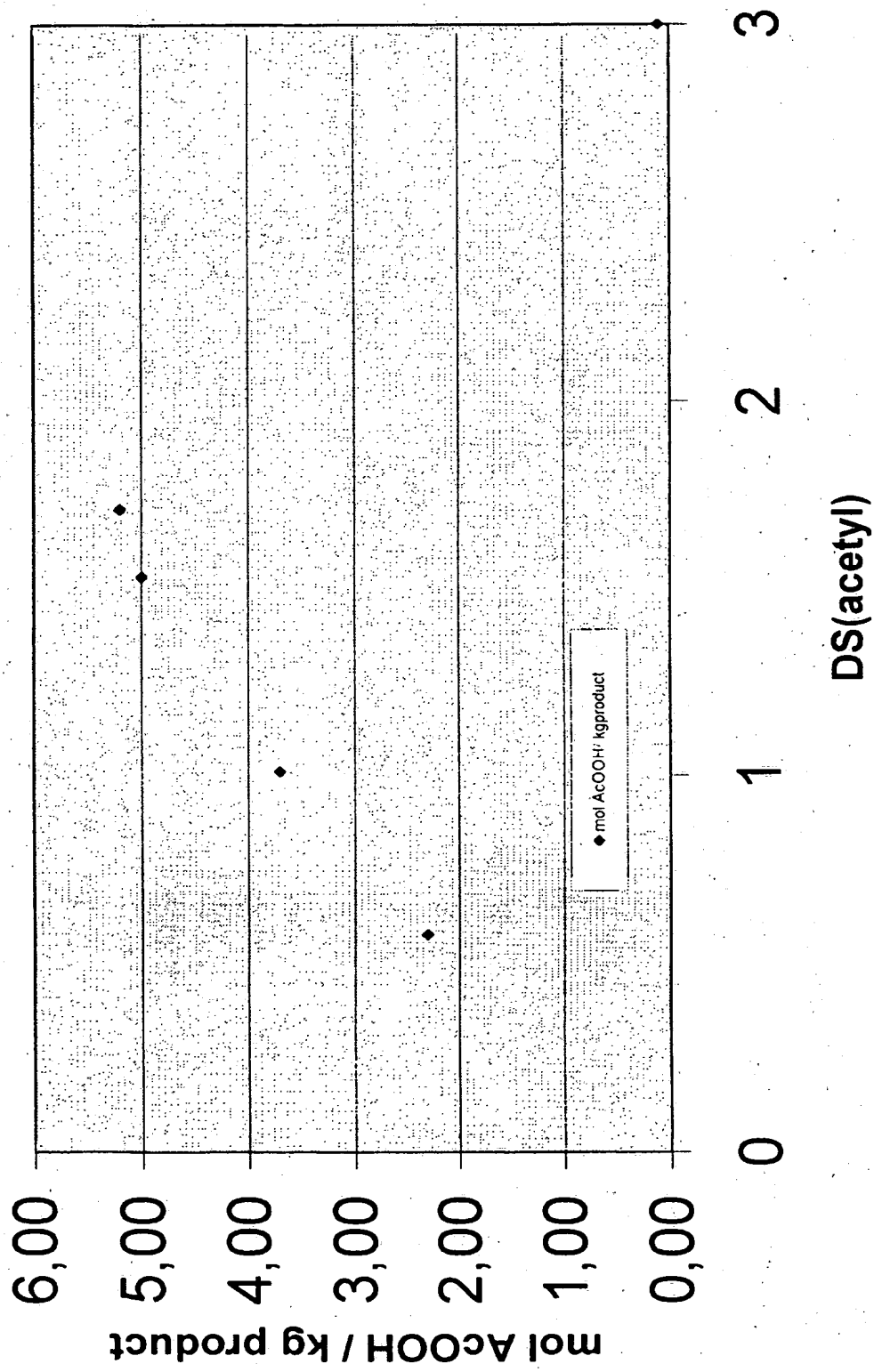

Bleekactivator op basis van inuline

De uitvinding heeft betrekking op de toepassing van fructaanderivaten als bleekactivator.

Voor het bleken van bij voorbeeld textielmaterialen in het wasproces is gewoonlijk naast een bleekmiddel, zoals een peroxide, percarbonaat of perboraat, een bleekactivator nodig. De meest toegepaste bleekactivator is tetraacetylethyleendiamine (TAED). Nadeel van TAED is dat het matig tot slecht biologisch afbreekbaar is, en dus een ongewenst bestanddeel in afvalwater is. Uit EP-A-492000 is de toepassing van geacetyleerde sucrose (substitutiegraad 4,5-7), in het bijzonder hexa-acetylsucrose, als bleekactivator bekend. Uit EP-A-731161 zijn geperacetyleerde suikerzuren (sucrose, maltose, lactose) met bleekactiverende werking bekend. In EP-A-814088 worden geacetyleerde carboxymethylinulinederivaten beschreven, die een bleekactiverende werking zouden hebben.

Gevonden is dat geacyleerde fructanen en fructaanderivaten uitstekend geschikt zijn als bleekactivator, met een met TAED vergelijkbare activiteit, en met een veel betere biologische afbreekbaarheid. De volgens de uitvinding toe te passen geacyleerde fructanen en fructaanderivaten hebben een gemiddelde substitutiegraad (in acylgroepen) van 0,4-2,5, bij voorkeur van 0,6-1,8 en liefst van 0,8-1,6. Verrassenderwijs blijkt de bleekactiverende werking van de geacyleerde inulinen volgens de uitvinding ook beter te zijn dan van de vergelijkbare geacyleerde carboxymethylinulinen volgens EP-A-814088. De acylgroepen van het geacyleerde fructaan volgens de uitvinding zijn bij voorkeur afgeleid van monocarbonzuren en kunnen acetyl-, propionyl-, butyryl- en hogere alkanoylgroepen (bij voorbeeld tot C12, in het bijzonder tot C6) en eventueel formyl-, alkenoyl-, pyruvyl- en benzoylgroepen e.d. zijn. Ook mengsels, bij voorbeeld van acetyl- en propionylgroepen, zowel binnen een molecule (acetylpropionylfructaan) als van verschillende stoffen (acetylfructaan en propionylfructaan), zolang de totale of gemiddelde substitutiegraad binnen de gestelde grenzen ligt.

Geacyleerd inuline is op zichzelf bekend uit EP-A-792888. De daarin beschreven geacyleerde inulinen hebben bij voorkeur een substitutiegraad van 0,5 of minder, en worden voorgesteld als oppervlakteactieve stof.

Onder fructanen worden hier alle oligo- en polysachariden verstaan die een meerderheid aan anhydrofructose-eenheden hebben. De fructanen kunnen een poly-

disperse ketenlengteverdeling hebben en kunnen al dan niet vertakt zijn. De fructanen omvatten zowel uit plantaardige of andere bron rechtstreeks verkrijgbare producten, als wel de producten waarbij door fractionering, enzymatische hydrolyse of synthese de gemiddelde ketenlengte is gewijzigd (verhoogd of verlaagd). De fructanen hebben een gemiddelde ketenlengte (= polymerisatiegraad, DP) van ten minste 3, oplopend tot circa 1000, in het bijzonder van 3 tot 60 monosacharide-eenheden. Bij voorkeur bevat het fructaan voornamelijk β-2,1-bindingen zoals in inuline. Inuline kan onder meer worden verkregen uit cichorei, dahlia en aardpeer.

Ook geacyleerde gereduceerde fructanen komen in aanmerking. Gereduceerde fructanen zijn fructanen waarvan reducerende eindgroepen (gewoonlijk fructose-groepen) zijn gereduceerd, bij voorbeeld met natriumboorhydride of met waterstof in aanwezigheid van een overgangsmetaalkatalysator.

Verder kunnen chemisch of fysisch gemodificeerde fructanen als basis voor geacyleerde derivaten dienen. De chemische modificatie komt bij voorkeur overeen met een substitutiegraad in de modificatie van minder dan 0,5 in het bijzonder minder dan 0,2. De modificatie kan bij voorbeeld een alkylgroep, hydroxyalkylgroep, carboxyalkylgroep, alkoxycarbonylalkylgroep, carboxylgroep, alkoxycarbonylgroep, aminoalkylgroep of acylaminogroep zijn.

Er zijn verschillende bereidingswijzen voor geacyleerde fructanen en fructaanderivaten beschikbaar. Reactie van carboxymethylinuline (DS 1,0) met een overmaat azijnzuuranhydride in aanwezigheid van natriumacetaat bij 120°C (analoog aan voorbeeld 12 van EP-792888) levert een product met een betrekkelijk laag gehalte aan acetylgroepen (DS acetyl = 0,78). Nagenoeg volledige acetylering in goede opbrengst (89%) kan worden bereikt door uitvoering van deze reactie bij 140°C (analoog aan de werkwijze van R.L. Whistler, *Methods in Carbohydrate Chemistry*, Vol. II, 211-212).

Gevonden is dat de reactie van fructanen en fructaanderivaten met azijnzuuranhydride in water bij gereguleerde pH een uitermate geschikte methode is voor de bereiding van partieel geacyleerde fructanen en fructaanderivaten. De pH tijdens de reactie wordt constant gehouden op een waarde tussen 7 en 9, bij voorkeur rond 8. De reactietemperatuur ligt tussen 0 en 80°C, bij voorkeur tussen 0 en 40°C. Deze methode resulteert in de vorming van partieel geacyleerde fructanen en fructaanderivaten in goede opbrengst (85-95%) en met een hoge reactie-efficiëntie (50-75%); de reactie-efficiëntie is gedefinieerd als de gemeten acyleringsgraad gedeeld door de op grond van de hoeveelheid

acyleringsmiddel berekende maximale acyleringsgraad (DS_{gem}/DS_{theor} x100%). In plaats van zuuranhydriden kunnen ook andere reactieve acylderivaten, zoals zuurhalogeniden, reactieve esters, vooral vinylesters zoals vinylacetaat en vinylpropionaat, voor de acylering worden toegepast.

Gebleken is dat de partiële acetylering van carboxymethylinuline (CMI) in een mengsel van azijnzuur, azijnzuuranhydride en zwavelzuur analoog aan EP-814088 slechts tot een product in lage opbrengst (41%) en met een lage reactie-efficiëntie (8%) leidt.

De eigenschap als bleekactivator is bepaald aan de hand van de hoeveelheid per-azijnzuur die uit het product kan worden vrijgemaakt. Gevonden is dat de eigenschappen als bleekactivator van de (partieel) geacyleerde fructanen en fructaanderivaten afhangen van de methode waarmee de acylering is uitgevoerd. De beste eigenschappen worden gevonden wanneer de acylering wordt uitgevoerd in water bij gereguleerde pH (Tabel 1).

De acetylering van CMI met azijnzuuranhydride, azijnzuur en zwavelzuur (EP814088) of azijnzuuranhydride en natriumacetaat bij verhoogde temperatuur levert producten op met een slechte oplosbaarheid in water en een geringe werking als bleekactivator.

Partiële acylering van CMI door reactie van CMI met azijnzuuranhydride in water met gereguleerde pH geeft producten met voldoende oplosbaarheid in water en betere resultaten in de bleekactivatortest. De oplosbaarheid in water is aanzienlijk hoger dan van overeenkomstige, volgens de stand van de techniek bereide producten. De uitvinding heeft eveneens betrekking op een dergelijke acyleringswerkwijze alsmede op de aldus verkrijgbare producten met een oplosbaarheid in water van ten minste 1 g/l.

Verrassenderwijs is gevonden dat hoe lager de substitutiegraad aan carboxymethylgroepen van partieel geacetyleerd CMI, hoe beter de werking als bleekactivator. Bij voorkeur wordt partieel geacetyleerd CMI met een substitutiegraad aan carboxymethylgroepen lager dan 0,2 gebruikt.

Van partieel geacetyleerd inuline (geen carboxylgroepen aanwezig) blijkt de oplosbaarheid van de verkregen producten goed tot een DS_{acetyl} = 2,0. De bleekactivatorwerking van deze verbindingen is beter dan partieel geacetyleerd CMI. De werking van partieel geacetyleerd inuline met een DS 1,7 benadert de werking van TAED en SORMAN. Een mogelijke verklaring voor deze resultaten is dat de bleekactivatorwerking bepaald lijkt te worden door de wateroplosbaarheid en de beschikbaarheid van de acetylgroepen. Het mol% gevormd peracetaat is een maat voor de beschikbaarheid van de

acetylgroepen. Een slechte wateroplosbaarheid geeft een lage beschikbaarheid van de acetylgroepen voor peracetaatvorming.

Tabel 1: Oplosbaarheid en bleekactivatorwerking van partieel geacetyleerd CMI, partieel geacetyleerd inuline, SORMAN en TAED op basis van hoeveelheid vrijgemaakt peracetaat.

DS (carboxymethyl)	DS (acetyl)	synthese-methode[1]	Oplosbaarheid (%)	gevormd per-acetaat (mol%)[2]	mol peracetaat / kg product
1	0,51	A	<0,1	39	0,8
1	1,05	B	<0,1	17	0,5
1	1,5	C	<0,1	20	1,0
0,2	0,66	D	>5	67	2,1
0,85	0,73	D	>5	51	1,4
1,5	1,12	D	>5	16	0,5
0	0,58	D	>5	73	2,3
0	1,01	D	>5	74	3,7
0	1,53	D	>5	73	5,0
0	1,71	D	>5	71	5,2
0	3,0	C	<0,1	4	0,1
0	0	-	10	-	-
1	0	-	50	-	-
vergelijking:					
TAED[3]	4,0	-	0,1	45	7,9
SORMAN[4]	6,0	-	0,1	44	6,0

1: A: AcOH/Ac_2O/H_2SO_4, 50°C, 3 uur; B: Ac_2O/NaOAc, 120°C, 4 uur; C: Ac_2O/NaOAc, 140°C, 4 uur; D: Ac_2O/H_2O, pH 8, 25°C.
2: 100x aantal mol gevormd peracetaat / totaal aantal mol acetylgroepen in product.
3: tetraacetylethyleendiamine
4: mengsel van peracetylsorbitol en peracetylmannitol (EP 525239)

In Tabel 1 is duidelijk te zien dat de aanwezigheid van carboxylgroepen in het inulinemolecuul een negatieve invloed heeft op de beschikbaarheid van de acetylgroepen voor peracetaatvorming. Hierdoor wordt de hoeveelheid peracetaat / kg product ook negatief beïnvloed.

Voor partieel geacetyleerd inuline geldt dat de beschikbaarheid van de acetylgroepen nagenoeg onafhankelijk is van de acetyleringsgraad tot een maximale DS van ongeveer 2. Dit betekent dat de hoeveelheid peracetaat per kg product nagenoeg evenredig toeneemt met de substitutiegraad (Figuur 1). Boven DS 2 neemt de oplosbaarheid en daarmee ook de beschikbaarheid van acetylgroepen voor peracetaatvorming weer af.

In vergelijking met TAED en SORMAN is de beschikbaarheid van de acetylgroepen in partieel geacetyleerd inuline wezenlijk hoger en derhalve wordt bij voldoende hoge acetyleringsgraad de peracetaatvorming per kg van die van TAED benaderd. De hoge beschikbaarheid van acetylgroepen in het partieel geacetyleerde inuline lijkt een unieke eigenschap van dit inulinederivaat te zijn. In figuur 1 is het aantal molen perazijnzuur per kg product tegen de DS_{acetyl} uitgezet.

Voorbeeld 1: *Acetylering van inuline, DS 1,0*

Aan 30 g inuline (185 mmol, cichorei, DP ≈ 10) werd 50 ml water toegevoegd, waarna het mengsel werd gehomogeniseerd en met 2M NaOH op pH 8 werd gebracht. Aan het mengsel werd bij kamertemperatuur 28 ml (296 mmol) azijnzuuranhydride toegedruppeld, terwijl de pH met een pH-stat onder toevoeging van 10M NaOH-oplossing op 8 werd gehouden. De temperatuur werd op 25°C gehouden. 15 minuten nadat alle azijnzuuranhydride was toegevoegd werd de oplossing met water verdund tot een volume van ca. 500 ml en werd de pH op 6 ingesteld. Na een nacht staan werd het neerslag afgefiltreerd. Het filtraat werd gezuiverd door nanofiltratie. Het filtraat van de nanofiltratie werd geconcentreerd (rotavapor) en het residu werd in een vacuümstoof bij 70°C gedroogd. Opbrengst: 36,25 g (95%) met een DS (substitutiegraad) in acetyl van 1,01. Reactie-efficiëntie: 63%. Het product had een oppervlaktespanning (1% g/g oplossing bij 30°C) van 47,78 ± 0,06 mN/m. Het product gaf een hoeveelheid peracetaat af (in mol%, bepaald volgens de procedure als beschreven in voorbeeld 9) van 74 mol%, ofwel 3,7 mol peracetaat per kg product.

Voorbeeld 2: *Acetylering van inuline, DS 0,5*

Voorbeeld 1 werd herhaald, echter met 15 ml (159 mmol) azijnzuuranhydride. DS: 0,51; opbrengst: 98%; reactie-efficiëntie 73%.

Voorbeeld 3: *Acetylering van inuline, DS 1,5*

Voorbeeld 1 werd herhaald, echter met 58 ml (613 mmol) azijnzuuranhydride. DS: 1,51; opbrengst: 84%; reactie-efficiëntie 53%.

Voorbeeld 4: *Acetylering van carboxymethylinuline*

Aan een oplossing van 150 g carboxymethylinuline (CMI, DS 0,88) werd in 3 uur 218 g azijnzuuranhydride toegedruppeld, terwijl de pH met 10M NaOH op 8 en temperatuur op 25°C werd gehouden. 15 minuten nadat alle azijnzuuranhydride was toegevoegd werd de oplossing met water verdund tot een volume van ca. 2,3 l en werd de pH op 6 ingesteld. Na een nacht staan werd het neerslag afgefiltreerd. Het filtraat werd gezuiverd door elektrodialyse. Het product werd geconcentreerd (rotavapor) en het residu werd in een vacuümstoof bij 70°C gedroogd. Opbrengst: 134,6 g (74%) met een DS (substitutiegraad) in acetyl van 1,2. Reactie-efficiëntie: 63%.

Voorbeeld 5: *Acetylering van inuline met NaOAc in azijnzuuranhydride bij 140°C*

Een suspensie van inuline (30 g) en natriumacetaat (3 g) in azijnzuuranhydride (150 ml) wordt verwarmd (140°C, 4 uur). Het warme reactiemengsel wordt uitgestort in ijswater (ca. 2 l) en een nacht geroerd. Het ontstane neerslag wordt afgefiltreerd en gedroogd aan de lucht. Opbrengst: 47,2 g (89%). DS acetyl: 3,0. Reactie-efficiëntie: 38%.

Vergelijkingsvoorbeeld A: *Acetylering van carboxymethylinuline in zuur milieu*

Aan een oplossing van CMI (DS 1,0; 10 g) in azijnzuur (50 ml, 100%) en geconcentreerd zwavelzuur (0,3 ml) wordt druppelsgewijs een mengsel van azijnzuuranhydride (25 ml) en azijnzuur (10 ml, 100%) toegevoegd en vervolgens geroerd (3 uur, 50°C). De oplossing wordt afgekoeld en gefiltreerd over een glasfilter. Het residu wordt gewassen (400 ml aceton/water (3:1)). Na verwijdering van aceton uit de gecombineerde filtraten (rotavapor) wordt het product ontzout d.m.v. nanofiltratie. Het retentaat wordt gevriesdroogd. Opbrengst 5,8 g (53 %). DS (acetyl): 0,49. Reactie-efficiëntie: 8 %.

Vergelijkingsvoorbeeld B: *Acetylering van CMI DS 1,0 met NaOAc en azijnzuuranhydride bij 120°C*

Een suspensie van CMI (10 g, DS 1,0) en natriumacetaat (0,5 g) in azijnzuuranhydride (50 ml) wordt verwarmd (120°C, 4 uur). Na afkoelen tot kamertemperatuur wordt het neerslag

verwijderd d.m.v. filtratie en het residu gewassen met azijnzuuranhydride. Het filtraat wordt geconcentreerd in vacuo (rotavapor). Vervolgens wordt het residu opgenomen in water en gevriesdroogd. Opbrengst 7,7 g (68%). DS acetyl: 0,78. Reactie-efficiëntie: 7%.

Vergelijkingsvoorbeeld C: *Acetylering van CMI (DS 1,0) met NaOAc in azijnzuuranhydride bij 140°C*

Voorbeeld 5 werd uitgevoerd met CMI (10 g, DS 1,0), 0,5 g natriumacetaat en 50 ml azijnzuuranhydride (50 ml). Opbrengst: 27,7 g (73%). DS acetyl: 1,5. Reactie-efficiëntie: 13%.

Voorbeeld 6: *Propionylering van inuline*

Aan 30 g inuline (185 mmol, cichorei, DP ≈ 10) werd 50 ml water toegevoegd, waarna het mengsel werd gehomogeniseerd en met 10M NaOH op pH 8 werd gebracht. Aan het mengsel werd bij kamertemperatuur 50 ml (388 mmol) propionzuuranhydride toegedruppeld, terwijl de pH op 8 en temperatuur op 25°C werd gehouden. Na een nacht staan werd het neerslag afgescheiden, met water gespoeld en afgefiltreerd. Het residu werd aan de lucht gedroogd. Opbrengst: 41,0 g (92%) met een DS (substitutiegraad) in propionyl van 1,41. Reactie-efficiëntie: 67%.

Vergelijkingsvoorbeeld D: *Nawerking voorbeeld 14 van EP-A-792888*

In 250 ml water werd 15 g (0,09 mol) inuline opgelost. Hieraan werden 12,3 ml (0,09 mol) propionzuuranhydride en 300 g ionenwisselaar Merck III (OH^--vorm) toegevoegd. Het mengsel werd onder roeren 24 u bij 40°C verwarmd. De oplossing werd afgefiltreerd (Büchner) en het filtraat werd ingedampt. Na toevoegen van 100 ml water werd nogmaals gefiltreerd. Het filtraat werd gevriesdroogd. De opbrengst was zo laag (158 mg) dat van karakterisering werd afgezien. Verschillende pogingen om het resultaat te verbeteren (a: herhalen; b: hars met water extraheren, extract ook indampen; c: hars spoelen met methanol, methanolfractie ook indampen; d: pH na reactie verlagen van 11 naar 6, gaven geen verbetering.

Voorbeeld 7: *Procedure bleekactivatortest*

Meng de volgende oplossingen:

- 15 ml 0,6 % waterstofperoxide-oplossing

- 10 ml verzadigde natriumpyrofosfaatoplossing
- 10 ml 0,05% EDTA-oplossing.
- Vul aan met demi water tot 100 ml en verwarm bij 30°C.
- Voeg het verwarmde mengsel toe aan een nauwkeurig afgewogen hoeveelheid (75-90 mg) bleekactivator in een bekerglas van 600 ml.
- Breng de pH op 11,6 met 0,1 M NaOH oplossing.
- Voeg na exact 4 minuten na de eerste toevoeging 30 ml 0,1 % katalase-oplossing toe.
- Breng de pH op 10,5 met 0,5 M zwavelzuuroplossing en koel de oplossing tot 0- 3°C.
- Voeg precies 6 minuten na de eerste toevoeging 15 ml 100% azijnzuuroplossing en 15 ml 10% kaliumjodide-oplossing toe.
- Titreer het vrijgekomen jodium met een 0,1 M thiosulfaatoplossing.

Uit de benodigde hoeveelheid thiosulfaatoplossing kan het mol % vrijgemaakt perazijzuur uit de bleekactivator worden berekend, waarbij 2 mmol thiosulfaat overeenkomt met 1 mmol gevormd perazijnzuur. De metingen zijn gecorrigeerd voor het verlies van perazijnzuur tijdens de meting. De correctiefactor voor dit verlies bedraagt 1,10. De resultaten van deze metingen staan in Tabel 1.

Conclusies

1. Toepassing van een partieel geacyleerd fructaan met een substitutiegraad aan acylgroepen van 0,4-2,5 en een substitutiegraad van ten hoogste 0,2 aan andere substituenten, als bleekactivator.

2. Toepassing volgens conclusie 1, waarbij het fructaan is geacyleerd met C_1-C_6-acylgroepen.

3. Toepassing volgens conclusie 1 of 2, waarbij het fructaan is geacyleerd met een substitutiegraad van 0,6-1,8.

4. Toepassing volgens een der conclusies 1-3, waarbij het fructaan een gemiddelde ketenlengte van 3-60, in het bijzonder van 4-30 heeft.

5. Toepassing volgens een der conclusies 1-4, waarbij de andere substituenten carboxymethylgroepen zijn.

6. Toepassing volgens een der conclusies 1-5, waarbij het fructaan inuline is.

7. Toepassing volgens een der conclusies 1-6, waarbij het fructaan is geacyleerd met acetyl- en/of propionylgroepen.

8. Werkwijze voor de bereiding van een geacyleerd fructaan of fructaanderivaat door acylering van het fructaan of derivaat daarvan met een reactief acylderivaat van een monocarbonzuur, *met het kenmerk*, dat men de acylering uitvoert in een waterhoudend medium bij een pH tussen 7 en 9.

9. Werkwijze volgens conclusie 8, *met het kenmerk* dat men de acylering uitvoert bij een temperatuur tussen 0 en 40°C.

10. Partieel geacyleerd fructaan verkrijgbaar met de werkwijze volgens conclusie 8 of 9, dat een oplosbaarheid in water van ten minste 1 g/l, in het bijzonder van ten minste 2 g/l heeft.

Uittreksel

De uitvinding betreft de toepassing van een partieel geacyleerd fructaan, in het bijzonder een partieel geacyleerd inuline, met een substitutiegraad aan acylgroepen van 0,4-2,5 en een substitutiegraad van ten hoogste 0,2 aan andere substituenten, als bleekactivator. De oplosbaarheid en werkzaamheid van deze derivaten is beter dan van vergelijkbare producten zoals volledig geacyleerde derivaten en gecarboxyleerde derivaten. De derivaten worden bereid door acylering in waterig milieu met gereguleerde pH.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/39 C11D3/22 D06L3/02 C08B37/18 C07H15/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D D06L C08B C07H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BERGHOFER E ET AL: "CHEMICAL MODIFICATION OF CHICORY ROOT INULIN" , STUDIES IN PLANT SCIENCE,NL,AMSTERDAM, ELSEVIER, VOL. VOL. 3, PAGE(S) 135-142 XP002031614	8,9
A	page 136, line 1 -page 137, line 5 page 137, line 35 -page 138, line 13	10
A	EP 0 792 888 A (SUEDZUCKER AG) 3 September 1997 (1997-09-03) cited in the application claims 1-11,15-18 examples 14,20 page 4, line 28 - line 30	1-4,6-10

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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29 September 2000	06/10/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Neys, P

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 01200 A (BEGHIN SAY ERIDANIA) 21 January 1993 (1993-01-21) claims examples page 1, line 16 - line 24 page 4, line 29 - line 34	1-9
A	EP 0 814 088 A (SUEDZUCKER AG) 29 December 1997 (1997-12-29) cited in the application claims example 8 page 2, line 47 -page 3, line 16 page 3, line 47 - line 58	1-7
A	WO 96 34934 A (SOLVAY INTEROX LTD) 7 November 1996 (1996-11-07) claims examples page 3, line 14 - line 29 page 6, line 14 -page 8, line 30 page 13, line 8 - line 14	1-7

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Information on patent family members

International Application No
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